

# IONIC LIQUID-DERIVED POLYMERS AS PROTEIN SCAFFOLDS

Simonida Grubjesic and Millicent A. Firestone

Materials Science Division, Argonne National Laboratory,  
9700 South Cass Avenue, Argonne, IL 60439

## INTRODUCTION

Industry is continually searching for improved enzyme performance and stability under harsh conditions. Enzyme stability is essential to numerous areas of protein usage including bioengineering to biocatalysis, biomolecular electronics. One of several approaches used in addressing this problem is the encapsulation of biomolecules into ordered materials (1). We have previously shown that imidazolium-based ionic liquids are capable of forming liquid crystalline mesophases (2-4). In this report we extend this work, producing a polymerized hydrogel that exhibits improved mechanical strength, while retaining the self-assembled structure. This anisotropic matrix is well suited for spatial encapsulation of proteins, which allows protein to keep its original 3-D structure and function in the gel. This straightforward, effective procedure for fabrication of durable and stable gels for protein encapsulation is a significant step forward in addressing issues such as protein stability, activity and accessibility in bio-catalysis.

## EXPERIMENTAL

The polymerizable ionic liquid monomer, 1-decyl-3-methylimidazolium acrylate (IL) was synthesized in high yield in a one step procedure from commercially available materials. Briefly, 1-decyl-3-methylimidazolium bromide was mixed with silver acrylate at room temperature and stirred under inert atmosphere for 3 days. The product was filtered through 0.45  $\mu\text{m}$  filter to remove silver bromide precipitate, freeze-dried and used without further purification. Polymerization of the monomer was carried out by UV treatment of aqueous homogeneous mixture of monomer IL and cross-linker/co-monomer poly(ethylene glycol)diacrylate (PEGDA). Structural ordering of the UV-cured gels was evaluated using both polarized optical microscopy and small-angle X-ray scattering (SAXS). Thermal properties were analyzed by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Percent incorporation of the IL into the gel was determined by Soxhlet extraction for prolonged period of time and NMR analysis of amount of recovered IL in extract by using the internal NMR standard.



Figure 1. A) Digital photograph of IL-PEG gel. B), C) Optical micrographs of IL-PEG gel.

Protein encapsulation was carried out using cytochrome c, a model water soluble protein. A homogeneous mixture containing IL, PEG co-monomer, water and Darocur 1173 photoinitiator was UV cured (365 nm, 5 min) to produce protein encapsulated gel. UV-vis spectroscopy was used to confirm protein encapsulation within gel matrix.

## RESULTS

The formed IL-PEG gels were found to be well-ordered self-supporting materials (Figure 1). The optical birefringence established self-assembly of the IL monomer in water was maintained in the formed gel (Figure 1). Furthermore, a high percentage of IL into the gel matrix was confirmed by Soxhlet extraction of the gel as well as thermogravimetric analysis. UV-vis spectroscopy confirmed that cytochrome c was successfully incorporated into the gel matrix and remained intact for extended periods of time at 4° C (Figure 2). In addition, reduction of cytochrome c in the gel matrix was determined to be successful upon addition of a reducing agent (Figure 2).

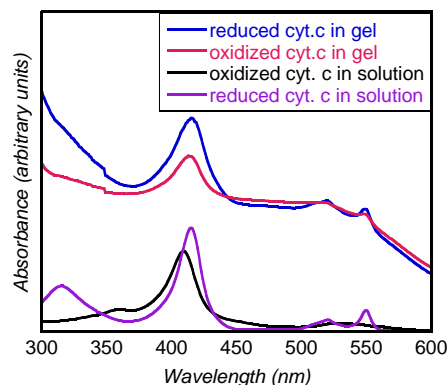


Figure 2. UV-vis scans of cytochrome c protein in both aqueous and gel media. Reversible redox process of cytochrome c in gel matrix was monitored by UV-vis scans.

## REFERENCES

1. Lester, C. L.; Smith, S. M.; Colson, C. D.; Guymon, C. A. *Chemistry of Materials* 15, 17, 3376 (2003).
2. Firestone, M. A.; Dzielawa, J. A.; Zapol, P.; Curtiss, L. A.; Seifert, S.; Dietz, M. L. *Langmuir* 18, (20), 7258 (2002).
3. Firestone, M. A.; Rickert, P. G.; Seifert, S.; Dietz, M. L. *Inorganica Chimica Acta* 357, 13, 3991 (2004).
4. Batra, D.; Hay, D. N. T.; Firestone, M. A., *Chemistry of Materials* 19, 18, 4423 (2007).

## ACKNOWLEDGMENTS

This work was performed under the auspices of the Office of Basic Energy Sciences, Division of Materials Sciences, U.S. Department of Energy, under contract number DE-AC02-06CH11357.